Monitoring and removal of residual phthalate esters and pharmaceuticals in the drinking water of Kaohsiung City, Taiwan

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HIGHLIGHTS

- Trace level (ng/L) of PAEs and pharmaceuticals could be detected in drinking water.
- The novel electromembrane system was capable of removing ECs from tap water.
- The removal mechanisms associated with electromembrane process were proposed.

ARTICLE INFO

ABSTRACT

This study monitored the occurrence and removal efficiencies of 8 phthalate esters (PAEs) and 13 pharmaceuticals present in the drinking water of Kaohsiung City, Taiwan. The simultaneous electrocoagulation and electrofiltration (EC/EF) process was used to remove the contaminants. To this end, a monitoring program was conducted and a novel laboratory-prepared tubular carbon nanofiber/carbon/alumina composite membrane (TCCACM) was incorporated into the EC/EF treatment module (collectively designated as "TCCACM-EC/EF treatment module") to remove the abovementioned compounds from water samples. The monitoring results showed that the concentrations of PAEs were lower in water samples from drinking fountains as compared with tap water samples. No significant differences were found between the concentrations of pharmaceuticals in the two types of water samples. Under optimal operating conditions, the TCCACM-EC/EF treatment module yielded the lowest residual concentrations, ranging from not detected (ND) to 52 ng/L for PAEs and pharmaceuticals of concern in the tap water samples. Moreover, the performance of the TCCACM-EC/EF treatment module is comparable with a series of treatment units employed for the drinking fountain water treatment system. The relevant removal mechanisms involved in the TCCACM-EC/EF treatment module were also discussed in this work.

1. Introduction

In recent years, the occurrence and fate of emerging contaminants (ECs) in the aquatic environment have been recognized as important issues in environmental chemistry [1–5]. ECs have been identified in surface water bodies [1,6–8] and sewage treatment plant effluents [6,9,10], at various stages of drinking water treatment plants [3,6,9–11], and even in finished drinking water [8,12]. Their measured concentrations range from ng/L to µg/L, which are much lower than those of normal macropollutants [3,6,10,13]. It is believed that many ECs may be chronically toxic to aquatic organisms and may pose risks to human health [14–16]. Another

characteristic is that some ECs, such as phthalate esters (PAEs) [12], pharmaceuticals and personal care products as pollutants (PPCPs) [17], do not need to persist in the environment to cause negative effects; their wide uses and transformation rates ensure their continuous presence in the environment.

The removal of ECs (e.g., PAEs, PPCPs, and endocrine disruptor chemicals, EDCs) from aquatic media is generally considered difficult. Many researchers [2,4,6,18] have found that municipal wastewater treatment facilities are incapable of removing these contaminants from sewage. Moreover, typical drinking water treatment systems can only partially remove this diverse group of chemicals from contaminated water sources. In recent years, the occurrences of ECs in drinking water have been widely reported [7–10,19,20]. To some degree, advanced oxidation processes (AOPs) [21–23] can transform many ECs into oxidation products. In addition, activated carbon adsorption [24–26], ultrafiltration (UF)

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[27–30], nanofiltration (NF) [30–33], and reverse osmosis (RO) [21,34,35] can partially remove ECs from aqueous solutions. However, due to the limitations of these treatment processes (i.e., removal efficiency, service life, space requirements, operational difficulty, etc.) and increasing demand for high water quality, it is imperative to develop new technologies and procedures for the removal of ECs from water.

Presently, the cost-effective removal of ECs and other co-existing contaminants from wastewater and drinking water remains a challenge. Given their ability to meet increasingly stringent drinking water regulations, membrane processes are widely used as a removal technology for ECs. Acero et al. [30] studied the removal efficiency of 11 selected ECs using UF and NF membranes. They found that the selected UF membranes had ECs removal efficiencies of below 50%. Yoon et al. [29] showed that while high removal efficiencies were obtained with the tested NF membranes, the PPCPs could not be eliminated completely. While NF and RO membranes are reportedly capable of removing PAEs and PPCPs, their removal efficiencies range from 10 to 99% [28,33–35]. Other studies [36,37] have also indicated the importance of the type of membrane and its properties when selecting a membrane for removing a wide range of ECs. The removal of these compounds through membrane processes is possible mainly due to size exclusion, membrane adsorption, and electrostatic repulsion [21,29,30,32]. In brief, separation by the size exclusion mechanism occurs when the EC molecules are larger than the membrane pores (i.e., they cannot pass through the pores). In general, size exclusion is mainly associated with NF and RO membranes. On the other hand, removal by electrostatic repulsion and adsorption occurs when the interactions between the membrane surface/pores and the ECs prevent the latter from entering the permeate stream. Membrane adsorption and electrostatic repulsion are believed to play a major role in the removal of ECs by UF membranes.

Because of having several benefits (e.g., lower energy requirements and high permeate fluxes), UF membranes are becoming fairly common in water treatment plants as replacements for media filters incapable of effectively removing ECs [27,29,30]. Conversely, NF and RO technologies enable medium to high removal of organic compounds such as ECs from water. Nonetheless, NF and RO still cannot achieve 100% removal of ECs from water. As a result, PAEs and PPCPs are commonly detected at trace levels in permeate [30,32,33]. Accordingly, in the real world there is a desperate need for fabricating membranes capable of yielding high ECs removal efficiency and high permeate flux. Surface modification of the UF membrane can help meet the aforementioned requirements. Moreover, using modified membranes coupled with a multifunctional filtration system is the key to improving the performance of membrane processes used for removing contaminants of emerging concern.

A novel simultaneous electrocoagulation/electrofiltration (EC/EF) method was developed by the first author of this paper [38]. Several studies used this patented method to treat various types of wastewaters containing nanoparticles [39–42]. Recently, Yang and co-workers [43,44] incorporated tubular carbonaceous/ceramic composite membranes into EC/EF treatment modules for evaluating and comparing the treatment performance for solutions containing pharmaceuticals. When an electric field strength of 30 V/cm, transmembrane pressure (TMP) of 98 kPa, and crossflow velocity (CFV) of 1.93 cm/s were employed, average removal efficiencies of over 95% for caffeine and sulfamethoxazole and about 78% for acetaminophen could be achieved [44]. In an earlier work [43], the same authors had also shown that over 96% of erythromycin and acetaminophen in sewage could be removed by the EC/EF process. Although the EC/EF process has demonstrated its capability in removing ECs from various aqueous solutions,

studies of using the EC/EF process to remove ECs from drinking water are still lacking.

In this study, a monitoring program was devised to monitor the concentrations of 8 PAEs and 13 pharmaceuticals in tap water and drinking fountain water samples collected from two buildings of a university campus from March 2011 to July 2013. To this end, the EC/EF treatment module was coupled with a tubular carbon nanofiber/carbon/alumina composite membrane (TCCACM) to evaluate the performance of this novel electromembrane process. In addition, an attempt was made to understand the contribution of each removal mechanism toward the relevant removal efficiencies of PAEs and pharmaceuticals of concern.

2. Experimental

2.1. Materials

Fine grains of alumina were used for preparing the tubular porous substrates of the TCCACM, using the extrusion method as reported by Yang and Li [41]. In general, the prepared tubular porous substrates (ID: 6 mm; OD: 10 mm) have a nominal pore size of about 1.0 mm. A plastic wrap of polyvinylidene chloride (PVDC; Kureha Chemical, Japan) was selected as the precursor for fabricating the intermediate carbon layers of the TCCACMs. Ferric sulfate (Panreac Quimica SA, Spain) was used as a catalyst precursor for the formation of the carbon nanofibers.

Methanol of high performance liquid chromatography (HPLC) grade was purchased from Mallinckrodt Baker, USA. Analytical grade formic acid, ammonium formate, erythromycin, acetaminophen, caffeine, diclofenac, tetracycline, 1,1-dimethylbiguanide hydrochloride, cephalexin, gemfibrozil, ibuprofen, ketoprofen, naproxen, sulfamethoxazole, di-n-butyl phthalate (DnBP), di-(2-ethylhexyl) phthalate (DEHP), and diisononyl phthalate (DiNP) were purchased from Sigma–Aldrich, USA. Analytical grade butyl benzyl phthalate (BBP) and di-n-octyl phthalate (DnOP) were purchased from Supelco, USA. Analytical grade diisodecyl phthalate (DiDP) and dimethyl phthalate (DMP) were purchased from AccuStandard, USA. Analytical grade diethyl phthalate (DEP) was purchased from Aladdin, China. Analytical grade triclosan was purchased from Alfa Aesar, USA. All the above-indicated chemicals supplied by American companies were of ACS (American Chemical Society) grade. Tables 1 and 2 list some general information about the selected compounds. Mixed standard working solutions (10 mg/L) were prepared by dilution of the standard stock solutions in methanol.

2.2. Collection of drinking water samples

Two types of drinking water samples, tap water and drinking fountain water, were obtained from two buildings of a university campus in southern Taiwan. These drinking water samples were collected mainly on Mondays, Wednesdays, and Fridays from March 2011 to July 2013. In total, 45, 10, and 32 samples were collected in 2011, 2012, and 2013, respectively. The sample collection procedures complied with the Taiwan EPA standard method NIEA W101.54A [45]. The drinking water samples were collected in 1 L amber Boston round bottles with Teflon-lined caps. Then, they were stored at 4 °C. To minimize the degradation of pollutants during the storage period, the samples were analyzed within the next 14 days.

2.3. Preparation and characterization of tubular carbon nanofiber/carbon/alumina composite membranes

2.3.1. Preparation procedures

The detailed procedures and conditions for preparation of the outside-in TCCACMs used in this work can be found elsewhere